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THE EVALUATION OF CREAMING AGENTS*

BY

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Summary

A description is given of the factors which should be considered in the evaluation of creaming agents indicating that the initial cost should be balanced against that of the service it gives and the influence it has on quality.

The efficiency of a creaming agent in service is measured by the optimum amount required under specified conditions of preparation and testing. A method of determining the optimum is described and some observations are made on the manner in which this is affected by the manufacture, preparation and keeping properties of a number of the commonly used creaming agents.

The theories advanced to explain the mechanism of creaming are reviewed and the general differences between creamed and centrifuged latex enumerated, but little information is available to enable discrimination to be made between latex prepared by different creaming agents.

The concentration of latex by means of creaming agents, generally known as the creaming process, constitutes one of the three methods now in commercial operation on the plantations. The process offers attractions to an estate on account of the low initial capital expenditure which is necessary to lay out on plant and equipment and the relatively low operating costs incurred in working the process.

The basis of the creaming process is well known and consists essentially of the addition to latex of materials which are hydrophylic in character and give aqueous solutions of high viscosity. They may be either vegetable gums or synthetic water-soluble materials such as polyvinyl alcohol and sodium polyacrylate.

The mechanism of the creaming process has been the subject of investigations by numerous technologists and many theories have been advanced as an explanation. These postulate either an increase in the size of individual particles due to their hydration by the creaming agent or an aggregation of the particles to form groups whereby the effective

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size and hence the buoyancy is increased. Baker (1937) has demonstrated experimentally that such aggregation does in fact take place resulting in a diminution of the Brownian movement. Stamberger (1929) has explained this on the theory that the creaming agent adsorbed on particles reduces their electric charge and lessens the repulsive forces, thereby permitting the particles to cohere into groups. Twiss (1938) has suggested that the viscous creaming agent forms a three-dimensional network system, which restricts the Brownian movement of the rubber globules but allows them to move until they form small groups. Clusters of globules continue to grow until they attain sufficient magnitude to break the network system, when they move upward and expel the entrapped aqueous creaming agent phase. This theory appears to fit the observed facts. Vester (1938) is of opinion that aggregation of the particles is due to a coacervate in the form of a viscous phase which is formed by interaction of the creaming agent and the serum substances. This viscous material envelops the particles and causes them to agglomerate. Bondy's (1939) explanation of creaming, based on observations made with sodium alginate, is that the creaming agent exerts a dehydrating influence on the stabilising protein of the rubber globules, thereby causing them to adhere to each other. His experiments indicated that the creaming agent is not adsorbed at the surface of the globules, in contrast to the assumption upon which several of the above theories are based.

From the above it is apparent that whereas general agreement exists that a creaming agent causes a reversible aggregation of the rubber globules with a decrease in their Brownian movement and an increase in their buoyancy, a divergence of opinion exists as to the causes of this aggregation. Many substance have been described in the technical and patent literature as being suitable for the production of these reversible aggregates but only a few have been utilised in estate work for the commercial preparation of creamed latex, all of which have been or still are subject to patent restriction.

The Rubber Research Institute of Malaya is called upon frequently to examine new creaming agents or modifications of existing ones and indications are given in this paper of the methods used and considerations involved in their evaluation. No attempt is made to give a comprehensive survey of materials now used as creaming agents with a view to their classification.

The amount of an efficient creaming agent required for creaming is relatively small and should not be more than 0.3 per cent. on the latex. Within this limit a large variation exists in the optimum amounts of different materials which in the case of one creaming agent may be four or five times that of another, dependent upon methods of manufacture and preparation. The cost of the creaming agent per lb. of rubber in the concentrated latex is not the only basis upon which a creaming agent should be evaluated. Whilst its ability to cause agglomeration of the globules is the chief factor, others which require consideration are its influence on the quality of the latex and its manipulative properties.

The relative rates of creaming of the commonly-used materials, gum tragacanth, Tragon seed gum, alginates etc. may be considered to be approximately the same if the optimum amount of each is used. Under these conditions the dry rubber content of the cream after a given period, for example four days, depends upon a number of factors including the initial dry rubber content of the field latex, the age and genetic strain of the trees from which the latex is obtained, the extent of prior agitation of the latex creaming agent mixtures, and the temperature of creaming. A latex is sometimes designated as a " poor creamer " but a more correct description would be that it is a " slow creamer." A slow creamer may be a latex whose dry rubber content is low or it may be a latex drawn from areas of young buddings of certain clones. An average field latex of 38 per cent. dry rubber content should give a cream of 58-60 per cent. after four days when creamed with the optimum amount of creaming agent, although eventually it may attain a value of 63-65 per cent after several months, the " dry rubber content-period of creaming " curve becoming asymptotic with a line parallel to the " period of creaming " axis. Bondy (*loc. cit.*) has pointed out that the closest packing possible with spherical globules of equal size could produce a latex having a dry rubber content of 67 per cent. The similarity of this value to that found in practice is of interest although the analogy between latex particles and spheres of equal size cannot be drawn since the globules of latex are certainly not uniform in size, they are probably not spherical and are moreover comprised of heterogeneous material.

The relative efficiencies of creaming agents cannot be determined generally by a comparison of the dry rubber contents of cream produced by equal weights of the creaming agents, nor by a comparison of the weights of creaming agent required to give the same viscosity solutions, although viscosity may be used as a guide. The most satisfactory method of determining the optimum amount of creaming agent was indicated by Twiss (*loc. cit.*) who observed the dry rubber contents of a series of creams prepared by the addition of solutions of creaming agent of varying strengths.

The optimum amount of a creaming agent may be defined as that required under specified conditions to give a " fairly clear " serum after creaming for four days, *i.e.* a serum which does not contain more than 2 per cent. of rubber. The " optimum amount " is an arbitrary value and cannot be stated as a specific value since it depends on the nature of the latex. The serum might be cloudy if freshly-tapped latex is creamed but clear if the latex is aged for a period. Hence the optimum amount applicable to all latex must lie within even wider limits than for a individual latex. If the serum is cloudy (too low a concentration of creaming agent) separation is not as complete as it should be and if the serum is clear (too high a concentration of creaming agent) it may be that the dispersion medium is too viscous and impedes the upward movement of the latex clusters, giving a large volume of cream of a low dry rubber content.

A convenient method used in the laboratories of the Rubber Research Institute for estimating quantitatively the optimum amount of creaming agent is to add 20 c.c. of the creaming agent solution to 200 c.c. of the latex in a separating funnel, allow the mixture after shaking to stand for four days, run off the serum and determine the dry rubber content of the cream for each strength of creaming agent. The concentration of the solutions of the creaming agents are usually stepped up in stages of 0.05 per cent. and a more exact value of the optimum amount may be then determined when the value within these limits is known.

Whilst, as already stated, the optimum amount of a material depends upon the conditions of the test and it is necessary therefore that this should be standardised as far as possible, it is affected to a greater degree by factors which may include variation in its method of manufacture, differences in the method of preparation of the solutions and the age of solutions. These factors are discussed below.

(*a*) *Influence of method of manufacture.*

Substances such as sodium alginate and methyl cellulose may be subjected to a degree of depolymerisation during their manufacture which has the effect of modifying the viscosities of their aqueous solutions although retaining the same chemical composition. We obtained through our colleagues of the London Advisory Committee samples of three grades of sodium alginate, known commercially as Manucol I, Manucol V and Manucol (Special High Grade Viscosity). The viscosities of 1 per cent. solutions of these materials prepared in the cold were found to be 11.6, 51.7 and 149.6 centipoises respectively when determined by the Höppler viscometer and it was observed that about half the amount of the high viscosity material was required for optimum creaming as compared with that of the low viscosity material. The viscosities of the optimum amounts (in gm.) dissolved in 100 c.c. water ranged from 2.21 to 4.24 centipoises, indicating that the viscosity of a creaming agent although giving an indication of the creaming power cannot be used as a close measure of its optimum. These results are shown in comparison with Tragon seed gum as a control in Table 1.

TABLE I

Creaming agent	Viscosity of 1% solution (centipoises)	Optimum amount of creaming of creaming agent (gm. per 100 c.c. latex)	Viscosity of solution of optimum amount (gm. per 100 c.c. of water) (centipoises)
Manucol I	11.6	0.105	2.21
„ V	51.7	0.075	3.79
„ Special High Grade Viscosity	149.6	0.050	4.24
Tragon seed gum	22	0.210	5.21

The above was demonstrated in another way by adjusting by trial the quantities of Manucol V, Manucol Special High Grade and Tragon seed gum to give solutions of the same viscosity as that of a 1 per cent. solution of Manucol I used as a control. The concentrations of the solutions and the approximately equal viscosities are shown in Table II. Only the control creamed satisfactorily.

TABLE II

Creaming agent	Concentration of solution (gm. per 100 c.c. latex)	Viscosity (centipoises)
Manucol I ..	1.00	11.6
„ V ..	0.38	11.5
„ Special High Grade Viscosity	0.20	11.1
Tragon seed gum ..	0.83	11.9

The results in Table I are of practical importance because they show that effective creaming can be obtained with only a relatively small amount of added material, one of the objections sometimes made against creamed latex being the presence of the creaming agent. The use of a small quantity of material also reacts favourably on the cost of creaming.

Samples of methyl cellulose from which solutions of different viscosity were obtained showed in contrast to sodium alginate solutions only small differences in creaming power. Solutions of different samples containing 2 per cent. of methyl cellulose had viscosities ranging from 24.7 to 84.8 centipoises but only small differences in creaming power were observed. The results are shown in Table III. The anomalous behaviour of methyl cellulose as a creaming agent has been commented upon by several investigators.

TABLE III

Dry rubber content of fresh latex .. *34.0 per cent.*

Ammonia content .. *1.19 per cent.*

Latex creamed for four days.

Sample	Viscosity of 2 per cent. solution (centipoises)	Creaming agent added to latex (gm. per 100 c.c.	Condition of serum	Cream dry rubber content per cent.	Serum dry rubber content per cent.
Methyl Cellulose No. 1 ..	24.7	0.15	Milky	51.3	4.3
		0.30	Slightly milky	53.3	1.9
Methyl Cellulose No. 2 ..	74.0	0.15	Milky	51.2	5.2
		0.30	Slightly milky	54.2	2.6
Methyl Cellulose No. 3 ..	84.8	0.15	Milky	53.0	5.5
		0.30	Slightly milky	54.7	2.7
Tragon Seed Gum ..	59.3	0.15	Clear	57.8	1.6

(*b*) *Effect of method of preparation of creaming agent solutions.*

Substantial differences in the viscosities of creaming agent solutions are produced by varying the methods of preparation. Tragon seed gum gives much more viscous solutions if it is boiled for a few minutes, whereas boiling has only a relatively small effect on the viscosities of tragacanth and alginate solutions, the viscosity being reduced. The viscosities of methyl cellulose solutions are also reduced, by boiling. Tamarind is of little value as a creaming agent unless the solution is boiled. The changes in viscocity of sodium alginate solutions on boiling are shown in Table IV. Viscosities were determined on 1 per cent. solutions before and after boiling for ten minutes.

TABLE IV

Sample	Viscosity of 1 per cent. solution	
	Cold	Boiled 10 mins.
	(Centipoises)	(Centipoises)
Manucol I ..	11.6	9.8
„ V ..	51.7	47.6
„ Special High Grade ..	149.6	127.3

The effect of boiling on viscosity and hence on the optimum amount is however more marked with solutions of Tragon seed gum than with solutions of any of the other creaming agents commonly used, that prepared by heating having a viscosity of approximately ten times that of a solution prepared at ordinary temperatures. Efficient creaming can be obtained therefore with an appreciably smaller amount of material. This is shown in Table V in which a series of experiments was made primarily to determine the effect on creaming of the ammonia contents of the latex. The results indicate the lower optimum of the boiled solutions, which lies between 0.1 and 0.2 per cent. since with 0.2 per cent. the serum is in each test " very clear ", indicating that the concentration is too high, whereas in the case of unboiled solutions the sera are in all cases " fairly clear ", indicating that the concentration used is in the neighbourhood of the optimum. As a result of many determinations the optimum amounts recommended in practice for good quality gums are 0.21 and 0.15 gm. for 100 c.c. of latex for unboiled and boiled solutions respectively.

TABLE V

Sample	Viscosity (centipoises)	Dry rubber content of Latex 37.8% Ammonia 0.5%				Dry rubber content of Latex 36.7% Ammonia 1.0%				Dry rubber content of Latex 35.0% Ammonia 1.5%			
		0.1% Tragon Seed Gum on volume of Latex		0.2% Tragon Seed Gum on volume of Latex		0.1% Tragon Seed Gum on volume of Latex		0.2% Tragon Seed Gum on volume of Latex		0.1% Tragon Seed Gum on volume of Latex		0.2% Tragon Seed Gum on volume of Latex	
		Condition of Serum	Dry rubber content Cream (per cent)	Condition of Serum	Dry rubber content Cream (per cent)	Condition of Serum	Dry rubber content Cream (per cent)	Condition of Serum	Dry rubber content Cream (per cent)	Condition of Serum	Dry rubber content Cream (per cent)	Condition of Serum	Dry rubber content Cream (per cent)
Unboiled	285.2	Milky	55.3	Fairly clear	56.8	Milky	56.8	Fairly clear	58.1	Milky	56.1	Fairly clear	58.3
Boiled solution	22.0	Slightly milky	58.3	Very clear	58.1	Fairly clear	58.0	Very clear	58.1	Slightly milky	56.7	Very clear	58.3

(*c*) *Effect of age of the solutions.*

The third factor which may affect the optimum for a given material is the age of the solutions. Whilst tragacanth, methyl cellulose and the Manucols give solutions which remain stable for some time, both Tragon seed gum and tamarind solutions rapidly become less viscous on storage, losing their ability to cream latex after two or three days. Tn Table VI viscosity changes on storage of boiled solutions of Tragon seed gum, together with the dry rubber contents of the respective creams prepared by means of these solutions, are shown. The solutions cannot be relied upon if they are more than two days old. The inability of these materials to retain their creaming power can be overcome by ammoniation or the addition of a small quantity of a preservative such as sodium pentachlorphenate. The initial viscosity is reduced on ammoniation (Table VII) and is followed by a gradual fall on storage. The creaming powers of a series of solutions ammoniated to different degrees were preserved for a period of at least four weeks' storage, at the end of which the solutions still creamed satisfactorily. Tamarind solutions (3 per cent.) also can be preserved satisfactorily with ammonia, the solutions retaining their creaming power for long periods. An interesting observation has been made that a boiled solution of Tragon seed gum is preserved more satisfactorily than an unboiled solution with 0.05 per cent. sodium pentachlorphenate, indicating that the boiling destroys the enzymes which ferment the carbohydrates present in these vegetable gums.

TABLE VI

Dry rubber content of latex .. *35.2 per cent.*

Ammonia .. *0.75 per cent.*

Sample	Viscosity: Freshly prepared (centipoises)	D.R.C. of cream (per cent)	Viscosity: 24 hours after preparation (centipoises)	D.R.C. of cream (per cent)	Viscosity: 48 hours after preparation (centipoises)	D.R.C. of cream (per cent)	Viscosity: 72 hours after preparation (centipoises)	D.R.C. of cream (per cent)	Viscosity: 120 hours after preparation (centipoises)	D.R.C. of cream (per cent)
I. Solution brought to Boiling ..	167.5	58.0	144.0	59.4	64.9	—	1.2	No creaming	—	—
II. Boiled 10 minutes	230.1	57.4	230.7	59.7	194.6	60.2	19.3	—	1.1	No creaming
III. Boiled ½ hour ..	182.5	58.2	182.4	59.8	151.3	61.0	88.1	—	1.3	No creaming

TABLE VII

Initial Viscosity (1 per cent. solutions)

Sample	Viscosity after storage for					Dry rubber content of Cream using 27 days-old solution: (per cent.)
	0 days (centipoises)	1 day (centipoises)	2 days (centipoises)	6 days (centipoises)	27 days (centipoises)	
I. No NH_3	133.0	144.3	95.1	Decomposed	Decomposed	
II. 0.1% NH_3	142.0	108.0	83.2	84.7	52.2	56.4
III. 0.3% NH_3	125.9	109.5	92.0	91.3	80.5	56.6
IV. 0.5% NH_3	117.1	108.4	97.0	93.5	77.4	57.2
V. 0.7% NH_3	123.0	117.7	108.9	92.3	72.3	57.7
IV. 1.0% NH_3	140.4	131.5	125.0	113.7	82.3	57.7

Uniformity of creaming agents.

Creaming agents of the vegetable gum type are subject to a variation in quality which is inseparable from all plant products. This is more apparent when materials of the same type are obtained from different sources, although variation has been observed in successive samples from the same source. Baker described the examination of a large number of samples of gum tragacanth from different sources and observed that some of these materials would not even cream at all. The market valuation usually gives an index of the creaming power and it has been observed that where a number of grades are supplied from any source the most satisfactory creaming material is generally the most expensive. The poor creaming gum tragacanths were invariably those having the lowest market valuation and gave solutions of low viscosity. We examined recently two samples of a proprietary grade of Tragon gum and then obtained two more samples from the same source. The two best quality samples both gave high viscosity solutions and had similar optima but the viscosities of second quality samples differed widely and their creaming capacity was also different. The viscosities of 1 per cent. solutions are shown in Table VIII which shows the necessity of checking up creaming agents either by means of a viscosity test or a creaming test.

TABLE VIII

Method of Preparation of Solutions	Best Quality Sample		Second Quality Sample	
	No. 1	No. 2	No. 1	No. 2
	(centipoises)	(centipoises)	(centipoises)	(centipoises)
Unboiled ..	30	37	24	10
Boiled ..	470	540	201	37

No data are available as to the extent of variation, in the case of the alginates and cellulose derivatives but in view of the technical control which can be exercised during their manufacture it should be possible to produce them in uniform qualities.

Keeping properties of gum.

The keeping properties of vegetable gums are of practical importance and precautions are necessary in storing them under tropical conditions of temperature and humidity, otherwise they become infected with a beetle of the family of the

Anobiidae which lives on the carbohydrates present in these materials. Although no ill-effects on the creaming efficiency have been observed these pests have to be sieved out before the creaming agent can be used. Tragon gum and tamarind are prone to this attack.

Effect of creaming agents on the quality of latex.

The evaluation of a creaming agent should take into consideration its effect on the quality of the concentrated latex but little information is available to discriminate between the quality of latex prepared by using different creaming agents, probably owing to the larger differences in quality which can be produced by a variation in manufacturing procedure and to the more general comparisons which are often made between creamed and centrifuged latex.

The chief factors responsible for the differences between creamed and centrifuged latex are (a) the state of agglomeration of the rubber globules differs in the two latices; (b) the insoluble non-rubber substances are removed during the process of centrifuging, whereas some may remain in creamed latex and the amount may be increased by impurities present in the creaming agent; centrifuged latex is invariably " clean ", whereas the cleanliness of creamed latex depends upon the procedure followed during preparation; (c) creamed latex may contain separated serum due to after-creaming; (d) centrifuged latex does not contain added viscous material necessary for creaming and therefore the viscosity is lower; the stability of centrifuged latex is lower probably for the same reason. Centrifuged latex is said to behave differently from creamed latex in maunfacturing processes and the explanation probably may be found in the above differences.

Since the mechanism of the creaming of latex is believed to be the same for all creaming agents, the nature of the material can have little effect in the case of (a) and (c). After-creaming will depend obviously on the period which elapses before the serum is run off and on the nature of the latex. A tendency has been observed for separation to continue for a longer period in the case of Manucol, which may be due to the higher stability of Manucol solutions as compared with those of the vegetable gums. The differences (b) and (d) are, on the other hand, affected by the type of creaming agent used. Reference has been made already to the smaller quantities of some creaming agents required for efficient creaming.

Probably (b) is the most important of the factors under discussion because it concern the preparation of a " clean " latex and the nature of the creaming agent used is therefore of importance in this connection. Latex deposits a sludge, consisting of hydrated inorganic and organic matter which settles on standing. The vegetable gums and methyl cellulose also contain insoluble matter of a highly flocculent nature whereas Manucol is practically completely insoluble. The amount of insoluble matter present in gums varies with the quality of the gums, being usually less in the better quality materials. The insoluble portion of gum is of no value as a creaming material. Table IX shows the amount of flocculent insoluble materials present in a number of gums, estimated by repeated centrifuging and washing of a solution made from a known weight of gum and then weighing the dried residue.

TABLE IX

Creaming Agents	Insoluble matter (per cent)
Tamarind ..	22.8
Tragon A ..	14.2
Schisa gum (Extra Quality) ..	14.6
„ „ (First Quality) ..	17.4
„ „ (Second Quality) ..	21.2

To prepare a " clean " latex it is necessary therefore to clarify the latex prior to creaming, either mechanically or by allowing it to stand for a few days, and to use as a creaming agent a material which gives a solution naturally free from insoluble matter or alternatively to clarify the creaming agent solution as is sometimes done in practice. Another method is to clarify the concentrated latex after preparation. It has been observed that very little deposition of flocculent matter occurs during the actual creaming process owing to the increased viscosity of the latex creaming agent mixture. It is apparent that a completely water-soluble creaming agent facilitates the preparation of a " clean " latex.

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